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Radian Corp., Austin, TX

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16. ABSTRACT This is one of a series of manuals addressing accidental releases of toxic chemicals. Methyl isocyanate (MIC) has an Immediately Dangerous to Life and Health (IDLH) concentration of 20 ppm, making it a substantially acute toxic hazard. Reducing the risk associated with an accidental release of MIC involves identifying some of the potential causes of accidental releases that apply to processes that use MIC. The manual identifies examples of potential causes and measures that may be taken to reduce the accidental release risk. Such measures include recommendations on plant design practices, prevention, protection, and mitigation technologies, and operation and maintenance practices. Conceptual cost estimates of possible prevention, protection, and mitigation measures are provided.

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PREVENTION REFERENCE MANUAL: CHEMICAL SPECIFIC: VOLUME 13: CONTROL OF ACCIDENTAL RELEASES OF METHYL ISOCYANATE

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SECTION 1
INTRODUCTION

The purpose of this manual is to provide technical information about the prevention of accidental releases of methyl isocyanate (MIC). This manual is one of a series of prevention reference manuals which includes general volumes on release prevention, protection and mitigation, as well as other selected chemical specific volumes. The manual addresses technological and procedural issues related to release prevention, associated with the storage, handling, and process operations involving MIC in the United States. This manual does not address uses of MIC not encountered in the United States.

This manual is intended as an introductory summary manual for persons charged with reviewing and evaluating the potential for releases at facilities that use, store, handle or manufacture MIC. It is not intended as a specification manual, and, in fact, the reader is referred to additional technical manuals and other information sources for more complete information on the topics discussed. Other information sources include manufacturers and distributors of MIC and technical literature on design, operation, and loss prevention in facilities handling toxic chemicals.

1.1 BACKGROUND

Increasing concern about the potential disastrous consequences of accidental releases of toxic chemicals resulted from the Bhopal, India accident of December 3, 1984, which killed approximately 2,300 people and seriously injured 30,000 to 40,000 more (1). In this accident, a toxic cloud of methyl isocyanate (MIC) was released from a storage tank at a Union Carbide of India pesticide plant.

While headlines of this incident have created current awareness of toxic release problems, there have been other, perhaps less dramatic, incidents in the past. Aside from the Bhopal accident, no fatalities or injuries have been reported due to accidental releases of MIC. However, cases have been documented concerning accidental releases or leaks of MIC. One such incident involving an accidental release of 45 gallons of MIC occurred on November 15, 1984 at FMC Corporation in Middleport, New York (2). This release was due to a pump failure and resulted in the evacuation of nearby areas including a school. Nine children and two adults, complaining of eye irritation, were treated at a local hospital.

These incidences have increased interest in reducing the probability and consequences of accidental toxic chemical releases that might harm workers within a process facility and people in the surrounding community. In February 1985, a Federal/State task force was formed to review and evaluate the design and operating practices of the MIC production and storage units at UCAPCO's (formerly Union Carbide's) Institute, West Virginia facility. The task force based its review primarily on information provided by UCAPCO in the form of documents, interviews, and plant inspections. The task force independently evaluated information using basic principles of engineering, physics and chemistry, standard industrial practices and technical judgment. The results of the investigation were helpful in compiling this document.

1.2 INDUSTRY PERSPECTIVE

In terms of industrial organic intermediate chemicals, MIC is a small volume chemical. The total production volume of MIC in 1984 was estimated at only 30 to 35 million pounds. At that time, MIC was produced at only one site and consumed at four other sites in the United States. Over 95 percent of MIC produced is used in the manufacture of pesticides and herbicides. Since the Bhopal release, however, the complexion of the MIC industry has changed.

Today MIC is no longer shipped by rail car or in drums. Even though there had been no incidents with the shipment of MIC, Department of Transportation regulations have tightened and customers no longer wish to handle shipments. This change has resulted in two facilities shutting down the units using MIC. Two other facilities have installed their own MIC producing units to provide the material as a captive intermediate. The remaining company moved its MIC user plant to Institute, West Virignia, to obtain MIC via pipeline transfer. As a result, there are no more bulk shipments of MIC in the United States.

Another impact of the Bhopal incident was the close inspection of the MIC-related facilities in the United States. In addition to the Task Force study of UCAPCO's Institute facility, the Occupational Safety and Health Administration (OSHA) inspected each plant. These investigations were thorough; they covered process operations, emissions controls, spill plans, and emergency response plans.

1.3 USES OF METHYL ISOCYANATE

MIC is primarily made from the reaction of methylamine and phosgene. Until recently, the Institute, West Virginia facility was the sole producer in the United States. In mid-1985 E.I. DuPont de Nemours began producing MIC at its facility in LaPorte, Texas. Total production of MIC in 1984 was estimated at 30 million to 35 millions pounds per year (3).

MIC is used as an intermediate in the manufacture of pesticides. Approximately 90 percent of the MIC produced in the United States is used in the production of four insecticides: 1) carbaryl (Sevin) manufactured by UCAPCO, 2) aldicarb (Temik) by UCAPCO, 3) carbofuran (Furadan) by FMC Corporation and 4) methamyl (Lannate) by DuPont. Additional insecticides produced using MIC include bendiocarb and oxamyl, and the herbicides methazole and tebuthiuron also use MIC in their production (3).

1.4 ORGANIZATION OF THE MANUAL

Following this introductory section, the remainder of this manual presents technical information on specific hazards and categories of hazards and their control for MIC. These are examples only and are representative of only some of the hazards related to accidental releases.

Section 2 discusses physical, chemical and toxicological properties of MIC. Section 3 describes the types of facilities which manufacture and use MIC in the United States. Section 4 discusses some process hazards associate with these facilities. Hazard prevention and control are discussed in Section 5. Section 6 presents a reference list. Appendix A is a glossary of key technical terms that might not be familiar to all users of the manual, and Appendix B presents selected conversion factors between metric (SI) and English measurement units.

SECTION 2
CHEMICAL CHARACTERISTICS

This section of the report describes the physical, chemical and toxicological properties of methyl isocyanate (MIC) as they relate to accidental release hazards.

2.1 PHYSICAL PROPERTIES

MIC is a highly volatile liquid at ambient conditions. At 68°F, it has a vapor pressure of 6.78 psia. At atmospheric conditions, MIC has a boiling point of 102.4°F and a freezing point of -112°F. Some of its common physical properties are listed in Table 2-1.

MIC is a colorless liquid with a sharp odor at concentrations greater than 2 ppm. Liquid MIC is slightly less dense than water having a density of 59.9 lb/ft^3.

The solubility of MIC in water is 60 lb/100gal at 68°F and the solubility of water in MIC is 9.7 lb/100 gal at 68°F. This solubility is only valid at very cool temperatures and low concentration, where the reactivity of water and MIC is not extreme. At higher temperatures and concentrations, solubility is unimportant since the compounds react quickly.

Another important property of MIC is its gas-phase density. Because MIC gas is about twice the density of air, it tends to stay close to the ground when released in still air. The incident at Bhopal clearly illustrates the dangers associated with large releases of MIC into still air. Terrain of the region may create pockets in which the heavier-than-air MIC can collect.

TABLE 2-1. PHYSICAL PROPERTIES OF METHYL ISOCYANATE

		Reference
CAS Registry Number	624-83-9	
Synonyms	Iso-, Cyanatomethane, MIC, Isocyanatomethane, Isocyanato-methane, Methyl Ester Isocyanic Acid	
Chemical Formula	CH_3NCO	
Molecular Weight	57.05	
Normal Boiling Point	102.4°F @ 14.7 psia	4
Melting Point	-112°F	4
Liquid Specific Gravity (H_2O = 1)	0.9599 @ 68/68°F	4
Vapor Specific Gravity (air = 1)	2.0 @ 102.4°F	5
Vapor Pressure	6.73 psia @ 68°F	4
Vapor Pressure Equation (Antoine's Equation)	$\ln P_v = 16.3258 - \frac{2480.37}{T - 56.31}$	6
where:	P_v = vapor pressure, mmHg T^v = temperature, kelvin (range: 230K to 340K)	
Liquid Viscosity	3.5×10^{-4} kg/meter/sec @ 32°F	4
Solubility in Water	60 lb/100 gal @ 68°F	4
Solubility of Water in	9.7 lb/100 gal @ 68°F	4
Latent Heat of Vaporization	223 Btu/lb @ 14.7 psia	4
Heat of Combustion	8,041 Btu/lb @ 77°F	4

2.2 CHEMICAL PROPERTIES AND REACTIVITY

MIC is listed in the Chemical Abstract Service (CAS) as Registry Number 624-83-9. MIC is one of the simplest and most reactive isocyanates, consisting of only a methyl group and an isocyanate group. The chemical structure is: $CH_3 - N = C = O$.

MIC is a highly flammable and reactive compound, particularly with compounds containing active hydrogen atoms. MIC and the related isocyanates are like aldehydes and ketones in their tendency to undergo addition reactions. The adjacent double bonds at the end of the molecule increase the instability of isocyanates, making them more reactive than their aldehyde and ketone counterparts. As a result of this instability, extreme care should be taken to avoid conditions that could result in fires, explosions and runaway reactions. MIC is usually stored and handled in dedicated stainless steel, nickel and glass-lined equipment. Other materials of construction might actually act to catalyze an undesirable reaction of MIC. In some instances, these reactions are so rapid and exothermic that they might lead to over-pressure releases of reactants. Water, at low concentrations in MIC, may begin to react slowly, at first. As the reaction progresses, however, the heat generated drives the reaction rate faster. In some cases, the heat generated from the water-MIC reaction is sufficient to initiate self-polymerization. In addition, tanks and reactors should not be filled to capacity to allow for possible expansions of the contents. Another precaution taken when handling and storing MIC is to blanket the contents of vessels with dry nitrogen.

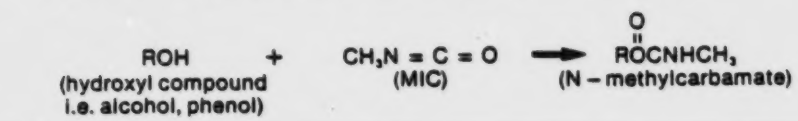
Due to the flammability of MIC, exposure to excess heat, sparks and flames should be avoided. MIC has a flash point of less than 0°F (open cup) and an autoignition temperature of 995°F (5). Flammability limits in air ranges from 5.3 to 26 percent by volume. Aside from MIC itself being highly toxic, other toxic gases such as hydrogen cyanide, nitrogen oxides and carbon monoxide could also be released as combustion products from a fire involving MIC.

As discussed above, MIC is an extremely active and unstable compound. From an industrial perspective, MIC is primarily reacted with hydroxyl compounds to form active agents used in pesticides manufacture. Figure 2-1 illustrates the major reactions involving MIC in the manufacture of pesticides. Examples of such reactions include the manufacture of carbaryl, aldicarb, carbofuran, and methomyl.

There are also two side reactions involving MIC that are undesirable in a commercial sense. A summary of these reactions are presented in Figure 2-2. If exposed to water, MIC can react to form carbon dioxide and water-soluble ureas or biurets. This reaction is slow at ambient temperatures. But, because of the heat generated from the reaction, the reaction rate increases rapidly to the point of violent boiling. The heat produced from such a reaction may result in excess pressure in process or storage vessels. The heat of reaction for MIC and water is 585 Btu per pound of MIC or 3,700 Btu per pound of water.

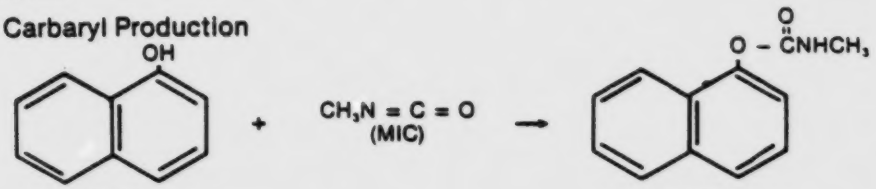
Another danger of MIC is its ability to react with itself in the presence of a catalyst to form trimethyl isocyanate. Though this reaction gives off less heat than the water-MIC reaction, it is also exothermic and can also cause a violent runaway reaction. The heat of reaction is 540 Btu per pound of MIC reacted. A variety of substances can catalyze this reaction. These catalysts include strong bases such as sodium hydroxide, sodium methoxide, and sodium acetate; and certain metal chlorides, such as ferric chloride and stannic chloride. For these reasons, MIC should at all times be kept out of contact with materials such as iron, steel, aluminum, zinc, copper, and tin since catalysts may be formed from these metals upon standing.

Methyl Isocyanate reaction with hydroxyl compounds:

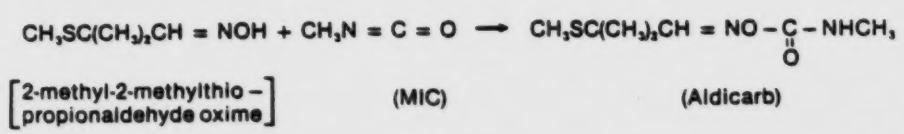


Examples:

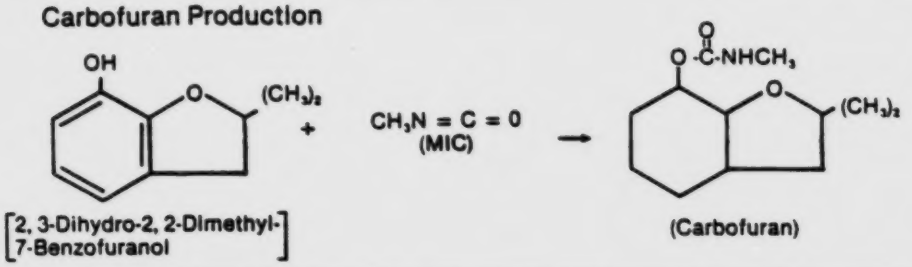
Carbaryl Production



Aldicarb Production



Carbofuran Production



Methomyl Production

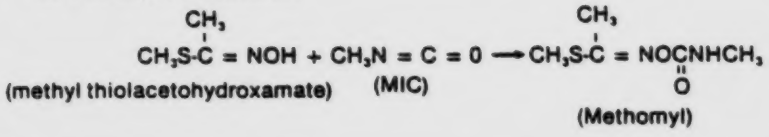


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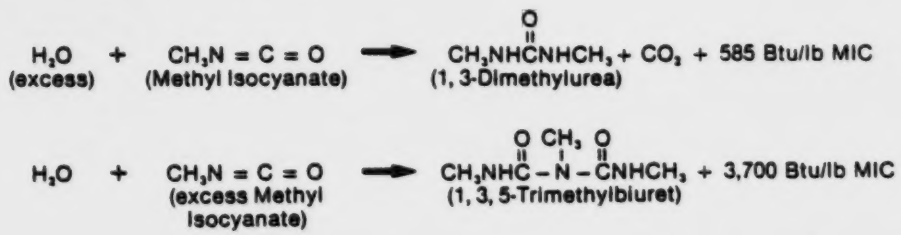
Figure 2-1. Major reactions of methyl isocyanate (MIC) with hydroxyl compounds.

Methyl Isocyanate reaction with water:


H2O (excess) + CH3N = C = O (Methyl Isocyanate) → CH3NHCNHCH3 + CO2 + 585 Btu/lb MIC (1, 3-Dimethylurea)
H2O + CH3N = C = O (excess Methyl Isocyanate) → CH3NHC – N – CNHCH3 + 3,700 Btu/lb MIC (1, 3, 5-Trimethylbiuret)

Methyl Isocyanate reaction with itself:

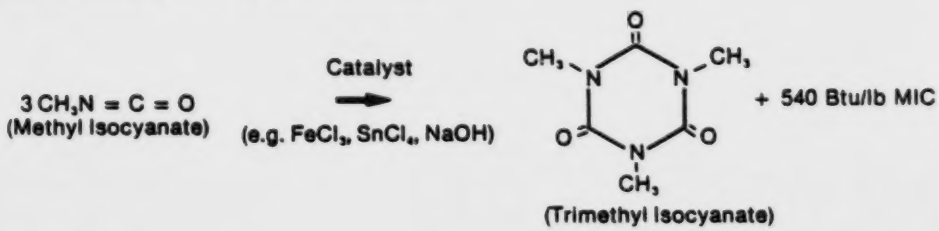


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Figure 2-2. Undesirable reactions of methyl isocyanate (MIC).

2.3 TOXICOLOGICAL AND HEALTH EFFECTS

Inhalation of MIC vapors causes irritation of the eyes, nose, throat and lungs. Furthermore, concentrations as low as 2 ppm have been reported toxic in humans (7).

Due to the difficulties associated with working with MIC, a limited amount of toxicology data has been collected for this compound. As with many toxic substances, toxicology data are primarily based on animal studies. One study on human subjects was conducted in West Germany in 1965 (8). In this study, human subjects were exposed to the gas for periods of one to five minutes. No effects of the gas were noticed by the subjects at 0.4 ppm. At 2 ppm, the subjects experienced irritation of the nose, throat, and eyes. As the MIC concentration was increased, irritation became worse until it was unbearable at 21 ppm. Based on this information, the American Conference of Governmental Industrial Hygienists (ACGIH) recommended workplace exposure limit of 0.02 ppm averaged over an eight-hour work shift. Table 2-2 presents a summary of some of the relevant exposure limits for MIC. Table 2-3 presents a summary of predicted human effects of exposure to various concentrations of MIC.

TABLE 2-2. EXPOSURE LIMITS FOR METHYL ISOCYANATE

Limit	Concentration (ppm)	Description
OSHA PEL	0.02	The current permissible exposure limit (PEL) average over an eight-hour work shift. (Occupational Safety and Health Administration)
ACGIH	0.02	A time-weighted eight-hour exposure to this concentration should result in no adverse effect for the average worker. (American Conference of Governmental-Industrial Hygienists)
IDLH	20	The concentration defined as posing an immediate danger to life and health (i.e., causes irreversible toxic effects for a 30-minute exposure).

Source: Reference 7.

TABLE 2-3. REPORTED HUMAN HEALTH EFFECTS OF EXPOSURE TO VARIOUS CONCENTRATIONS OF METHYL ISOCYANATE

ppm	Predicted effect
2	Irritations in the nose and throat, eyes begin to water
2	Lowest reported toxic concentration for humans
Greater than 2 ppm	Odor threshold
21	Exposure is unbearable

Source: Reference 8.

SECTION 3
FACILITY DESCRIPTIONS

This section provides brief descriptions of the manufacture and uses of methyl isocyanate in the United States.

3.1 METHYL ISOCYANATE MANUFACTURE

Prior to 1985, all the MIC produced in the United States was manufactured by Union Carbide in Institute, West Virginia. MIC was then stored for consumption in Union Carbide's own pesticide production or shipped to other companies. However, since 1985, numerous changes have been made concerning the manufacture, shipping and consumption of MIC. Table 3-1 presents a listing of facilities either producing or consuming MIC in the United States. MIC is also produced outside of the United States in Japan, Germany, Israel, Taiwan, and Korea.

In late 1986, Union Carbide sold substantially all of its worldwide agricultural products business, including its Institute plant, to Rhone-Poulenc Inc. (9). Union Carbide Agricultural Products Company (UCAPCO), a wholly-owned subsidiary of Rhone-Poulenc, continues to operate the Institute MIC unit. Two facilities which previously purchased MIC from Union Carbide are currently manufacturing their own MIC. These facilities are owned by E.I. DuPont de Nemours in LaPorte Texas, and Sandoz Ltd. (formerly Velsicol) in Beaumont, Texas. The two facilities manufacture MIC as a captive intermediate that is used as quickly as it is produced with no storage. A third company, FMC, has relocated its operations that consume MIC from Middleport, New York to Institute, West Virginia. MIC is now transported from UCAPCO by pipeline to FMC's new facility where it is converted to carbofuran. Thus, all three companies that previously received MIC shipments from Institute, West Virginia, have eliminated shipping and storing operations, reducing some potential for accidental releases.

TABLE 3-1. FACILITIES PRODUCING OR USING MIC IN UNITED STATES

Company	Location	Use of MIC
UCAPCO	Institute, WV	MIC production, pesticides production, MIC sale (to FMC)
E.I. DuPont	LaPorte, TX	MIC intermediate to Lannate (methomyl) and Vydate (oxamyl)
Sandoz Ltd.	Beaumont, TX	MIC intermediate to Probe (methazole)
FMC Corp.	Institute, WV	Carbofuran production

3.1.1 MIC Manufacture by UCAPCO (10,11,12)

A simplified process diagram of Rhone-Poulenc's MIC production process is presented in Figure 3-1. MIC is produced at UCAPCO by reacting anhydrous monomethylamine with phosgene in a high temperature vapor-phase reaction. MIC is produced by the following two-step chemical reaction.

(1) $COCl_2$ + CH_3NH_2 ----> $CH_3NHCOCl$ + HCl

Phosgene; Monomethylamine; Methylcarbamoyl Chloride; Hydrogen Chloride.

(2) $CH_3NHCOCl$ ----> CH_3NCO + HCl

Methylcarbomoyl Chloride; Methyl Isocyanate (MIC); Hydrogen Chloride

The first reaction involves an exothermic reaction between anhydrous monomethylamine and phosgene in a one-to-one ratio. Excess phosgene is used to insure complete reaction of the monomethylamine to methylcarbamyl chloride and hydrogen chloride.

The products from this first reaction are then quenched with chloroform and fed to a stripping column for recovery of the unreacted phosgene. The phosgene-rich stream is taken off the top of the stripper and recycled. The bottoms from the stripper are fed to a pyrolyzer. Heat converts methylcarbamoyl chloride to MIC and hydrogen chloride. A condenser is then used to remove hydrogen chloride gases, leaving an MIC-rich liquid stream. This stream consists mostly of MIC, methylcarbamoyl chloride, chloroform and small amounts of residues. MIC is separated in the upper part of a still. Methylcarbamoyl chloride, chloroform, residues and some MIC are recycled from the bottom of the still back to the process. HCl removed from the reactor and pyrolyzer are sold to a nearby chemical company where it is reused.

MIC from the top of the still is temporarily stored as a liquid in one of three 14,000-gallon storage tanks. MIC in these tanks is maintained at or

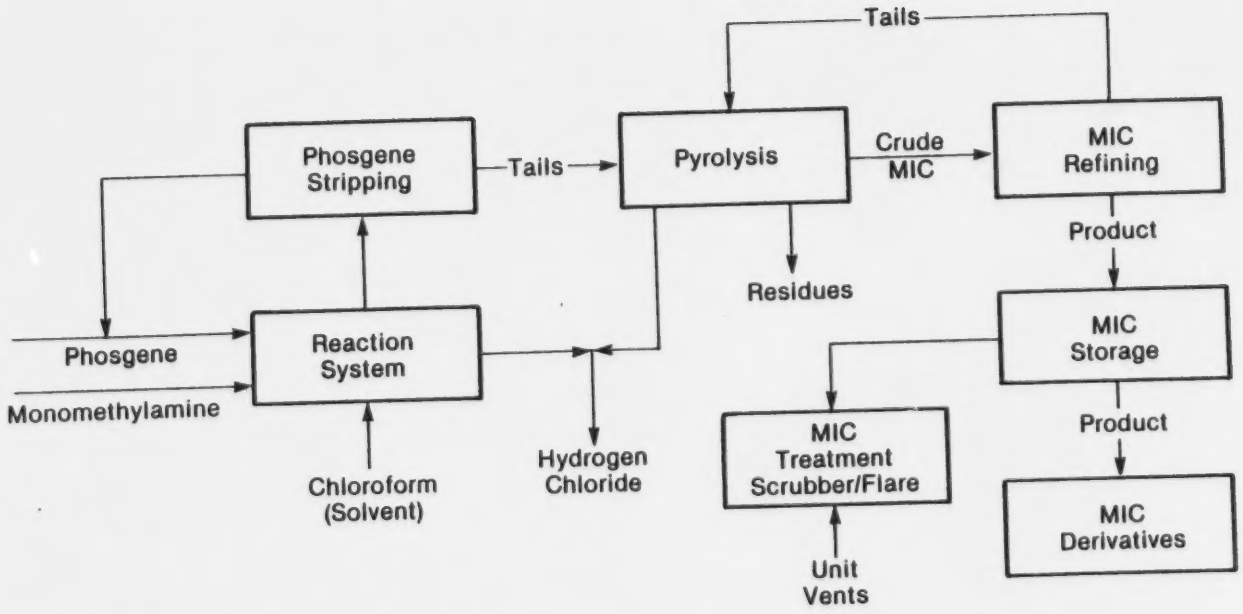

Figure 3-1. Methyl isocyanate (MIC) production process at UCAPCO's Institute, West Virginia facility.

below 0°C using a chloroform refrigeration system. MIC in intermediate storage is then sampled to assure compliance with product specifications. MIC not meeting product specifications is either reprocessed or destroyed. Refined MIC is transferred to one of three 30,000-gallon underground storage tanks. Tanks are pressurized and equipped with pressure relief valves set at 30 psig. Process tanks are equipped with pressure relief valves set at 20 psig.

Due to the extreme reactivity of MIC with water, a dedicated nitrogen system is used to blanket tanks and process equipment, reducing the potential for contact with water vapor. All process equipment in the MIC unit is dedicated to MIC production only. All process vents are vented to a scrubber followed by a flare to insure destruction of hazardous emissions to the atmosphere. The control efficiency of the scrubber and flare are estimated at 99.9 percent and greater than 98 percent, respectively. (10)

3.1.2 MIC Manufacture by DuPont (13,14,15,16)

DuPont began producing MIC in mid-1985. As shown in Figure 3-2, the method used to produce MIC at DuPont is significantly different from the process used by UCAPCO. In this process, monomethyl formamide is the raw material. Monomethyl formamide is oxidized using a mixture of natural gas and air at low pressure and high temperature followed by reaction with air at 1,000 - 1,200'F to produce vapor-phase MIC. The process is designed so that no more than two pounds of MIC are in the process at any one time. Nitrogen is used to avoid operating the converter in the explosive range of monomethyl formamide and air. From the converter, vapor-phase MIC is used to produce methomyl (Lannate). A description of the methomyl production is presented in Section 3.2.2.

Emission vents from the MIC process are routed to a caustic scrubber which neutralizes any MIC that does not react to product. If the product reaction stops, caustic will also neutralize all of the MIC being produced until feeds to the MIC production step can be stopped. Gases from the

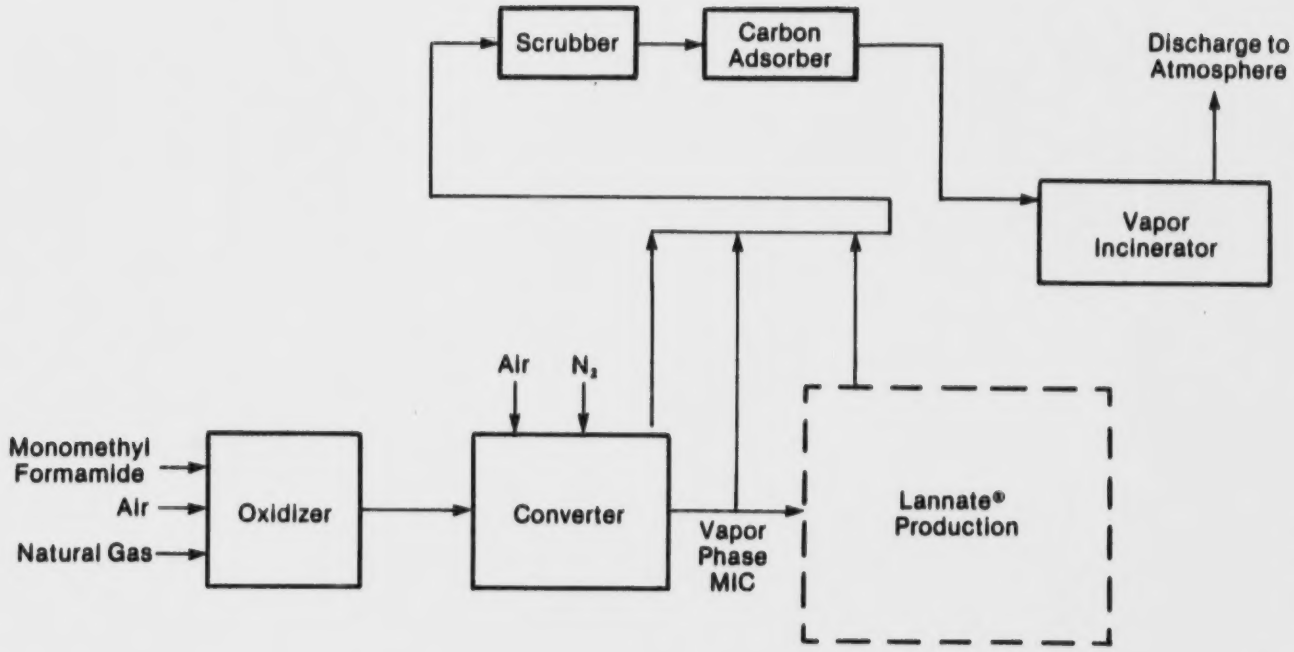

Figure 3-2. Methyl isocyanate (MIC) production process at DuPont's LaPorte, Texas facility.

scrubber are routed in series to the plant's carbon adsorber and vapor incinerator. As with the scrubber, the vapor incinerator is also designed to destroy the entire quantity of MIC produced, should the product reaction stop and the scrubber fail. All vessel and equipment containing MIC are also equipped with either relief valves and/or rupture discs. These relief devices are vented to the vapor incinerator. Liquid waste streams from the process are either burned in the plant's incinerator or treated in the plant's wastewater treatment facilities.

3.1.3 MIC Manufacture by Sandoz Ltd. (17,18)

MIC produced at Sandoz Ltd in Beaumont, Texas is consumed immediately at a rate of 2 lb/min in the production of methazole (Probe). Like the UCAPCO process, MIC is produced from the reaction between monomethylamine and phosgene. Vent gases from production processes are sent to two caustic scrubbers connected in series followed by a flare. Control devices are designed to destroy all MIC produced should the entire output from the MIC generator be diverted. Equipment containing MIC are also equipped with pressure relief devices which are vented to the scrubbers and incinerator. Since the MIC is consumed as it is produced by Sandoz Ltd., storage of the chemical is not necessary.

3.2 METHYL ISOCYANATE CONSUMPTION

A list of products manufactured worldwide using MIC is presented in Table 3-2 (19). This table also indicates trade names and companies responsible for the specified product. Of these products, many are not currently being produced or are produced outside of the United States. Out of an estimated 30 million to 35 million pounds of MIC consumed in the United States per year, 90 percent is consumed in the production of four products. These products are 1) carbaryl manufactured by UCAPCO in Institute, WV; 2) aldicarb manufactured by UCAPCO in Institute, WV; 3) carbofuran manufactured by FMC Corporation in Institute, WV; and 4) methomyl manufactured by DuPont in LaPorte, TX. Additional products produced in the United States include

TABLE 3-2. PRODUCTS MANUFACTURED USING METHYL ISOCYANATE

Product	Trade Name	Company
Aldicarb	Temik	Union Carbide
Aminocarb	Matacil	Bayer
Bendiocarb	Ficam	Fisons, Ltd.
Benzthiazuron	Gatnon	Bayer
Bufencarb	Bux	Chevron
Butocarboxim	Drawin 755	Wacker-Chemie
Carbaryl	Sevin	Union Carbide
Carbofuran	Furadan	FMC Corporation
Dioxacarb	Famid	Ciba-Geigy
	Elocron	Ciba-Geigy
Ethiofencarb	Croneton	Bayer
Formatanate	Dicarzol	Schering AG
Methabenzthiazuran	Tribunal	Bayer
Methazole	Probe	Sandoz
	Paxilon	Fisons
	Bioxone	Sandoz
	Tunic	Sandoz
Methiocarb	Mesuriol	Bayer
	Draza	Bayer
Methomyl	Lannate	DuPont
	Nudrin	Shell Chemical
Methylcarbamate 3,4-Xylyl	Meobal	Sumitomo Chemical
Methylcarbamate 3,5-Xylyl	Macbal	Hokko Chemical
Methylcarbamate	Broot	Union Carbide
Mexacarbate	Zectran	Dow Chemical
Nitrilacarb	Accotril	American Cyanamid

(Continued)

TABLE 3-2. PRODUCTS MANUFACTURED USING METHYL ISOCYANATE (Continued)

Product	Trade Name	Company
Oxamyl	Vydate	DuPont
Promecarb	Carbamult	Schering AG
Propoxur	Baygon	Bayer
	Blattanex	Bayer
	Unden	Bayer
	Sendran	Bayer
	Suncide	Mobay
	Tendex	A. H. Robins
	Undene	Mobay
Thiazfluron	Erbotan	Ciba-Geigy
Thiofunox	Decomox	Diamond Shamrock
Trimethylphenyl	Landrin	Shell

Source: Reference 19.

methazole (Sandoz, Ltd.), mexacarbate (UCAPCO), oxamyl (DuPont), and trimethylphenyl methylcarbamate (UCAPCO).

Prior to the Bhopal incident, methyl isocyanate was shipped to various facilities using it as the raw material in producing pesticides. Union Carbide shipped MIC to its Woodbine, Georgia plant producing aldicarb, to FMC's Middleport, New York Plant producing carbofuran, to other similar U.S. companies, and overseas to its affiliate operations. While shipping regulations had been strict with regard to containers and handling procedures, MIC is no longer shipped via tank car, tank truck, drum, or carboy. Some laboratory samples of no more than one gallon each are shipped. To eliminate bulk shipments of MIC, operations requiring MIC have 1) installed MIC production capacity, 2) moved to the production source of supply, or 3) shut down.

3.2.1 MIC Consumption by UCAPCO (11,19)

UCAPCO uses MIC in several processes at its Institute, WV facility. These processes include the manufacture of carbaryl (Sevin), aldicarb (Temik), mexacarbate (Zectran), trimethylphenyl methylcarbamate (Broot), and methomyl (Nudrin) which is marketed by Shell Chemical.

Approximately half of the MIC produced by UCAPCO is used in the manufacture of carbaryl. Figure 3-3 illustrates the process diagram for carbaryl production. Used since 1983, this is a rather simple process involving the reaction of MIC with β-naphthol. The reaction produces a high yield of carbaryl and no hazardous by-products. Reaction vessels in this process are vented to a flare for destruction of unreacted MIC. Prior to 1973, carbaryl was produced by the alternate reaction of β-naphthol with phosgene to form chloroformate. Carbaryl was then produced from the reaction of chloroformate and methylamine.

Aldicarb is the second largest usage of MIC at the Institute plant. A typical process diagram for aldicarb production is illustrated in Figure 3-4. Until recently, aldicarb was manufactured at UCAPCO's Institute, West Virginia

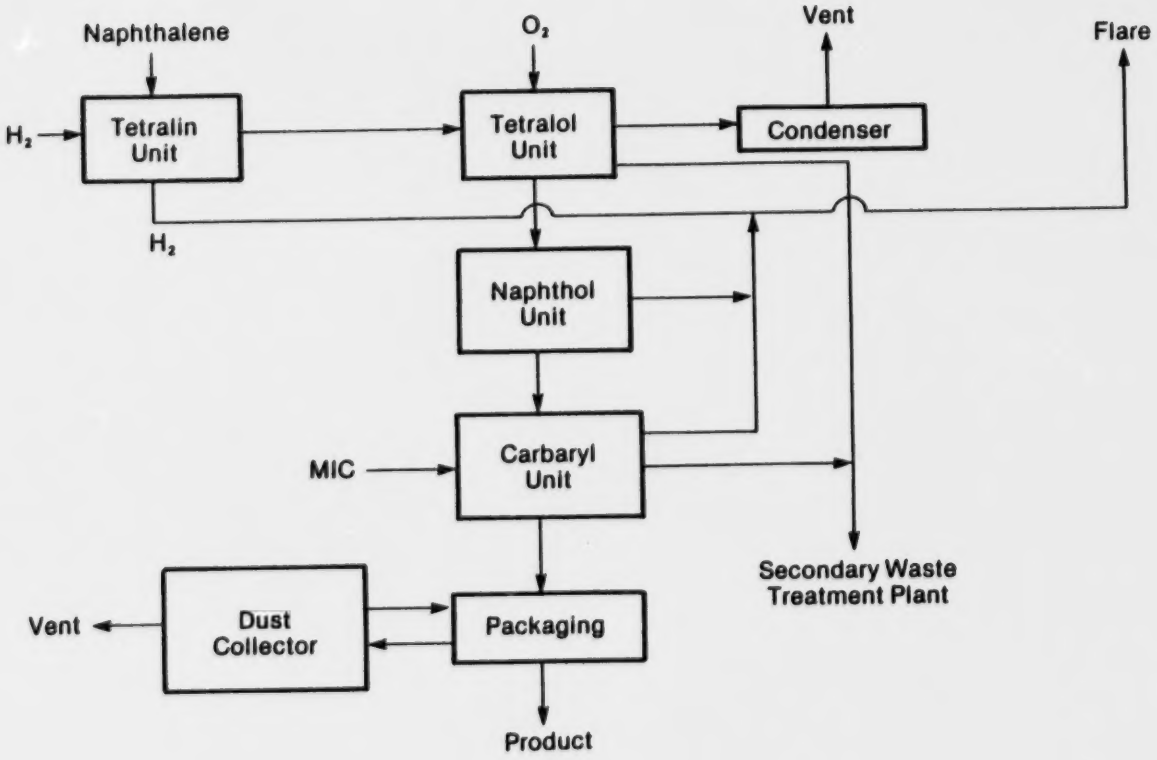

Figure 3-3. Carbaryl (SEVIN®) production at UCAPCO's Institute, West Virginia facility.

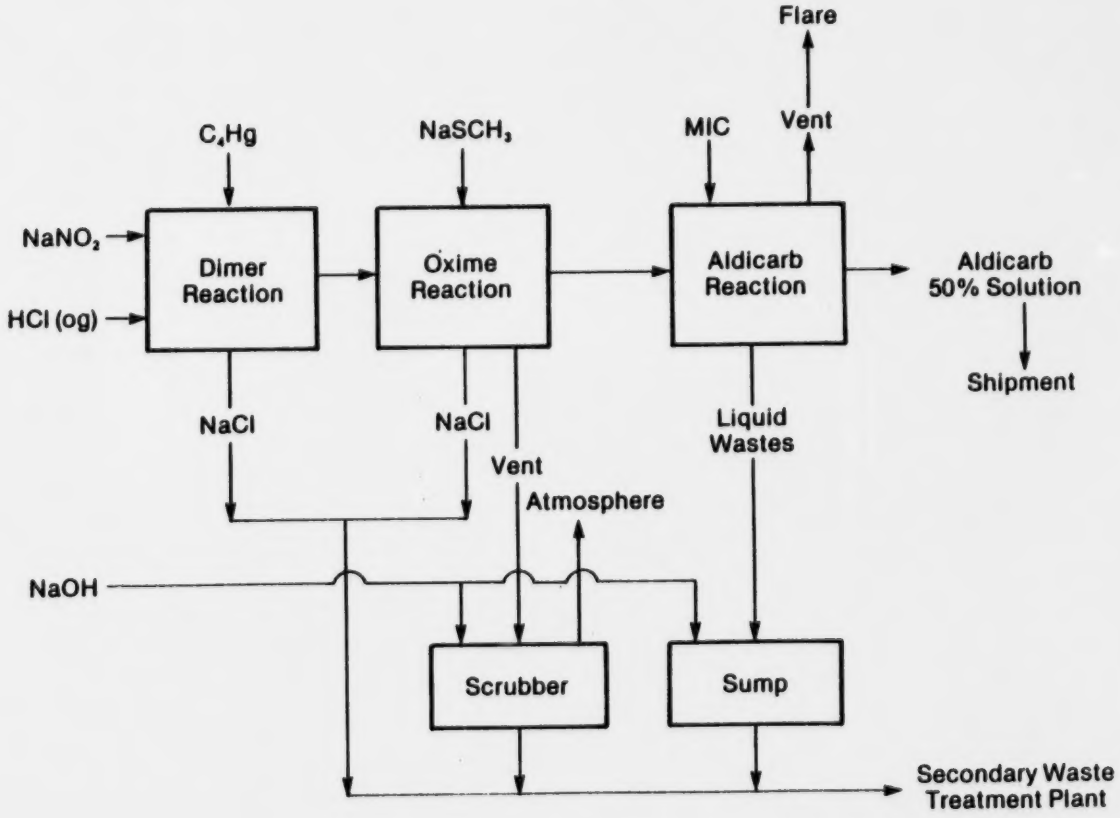

Figure 3-4. Aldicarb (Temik®) production at UCAPCS's Institute, West Virginia Facility.

and Woodbine, Georgia facilities. However, since 1986, aldicarb has been manufactured exclusively at the Institute, West Virginia facility. Aldicarb is produced by the reaction between MIC and 2-methyl-2-methylthio-propionaldehyde oxime. The aldicarb unit is vented to a scrubber.

A third pesticide is also produced at the Institute facility. Manufactured by UCAPCO, methomyl is marketed by Shell under the trade name Nudrin. No information has been found concerning this process.

3.2.2 MIC Consumption by DuPont (11,19)

DuPont's production process for methomyl is illustrated in Figure 3-5. In this process, MIC is reacted with methyl thiolacetohydroxamate at approximately 77°F in a one-to-one molar ratio. Methylene chloride is used as a solvent in this reaction. Any MIC emitted from the reactor is vented to a caustic scrubber where it is neutralized. Effluent gas from the scrubber is compressed and condensed to recover the methylene chloride for reuse in the process. The gas from the recovery system is sent to a carbon adsorber and vapor incinerator in series for ultimate destruction of residual volatile organics. Liquid effluent from the caustic scrubber is neutralized in the plant biological treatment facilities.

3.2.3 MIC Consumption by FMC (11,19,20)

Prior to the Bhopal incident, MIC was shipped to FMC's Middleport, NY facility for conversion to technical grade carbofuran. FMC has constructed its own facility at Institute, West Virginia. The carbofuran is now shipped by rail to the Middleport facility for additional processing.

The production process for carbofuran is illustrated in Figure 3-6. Carbofuran is produced by the exothermic reaction of 2,3-dihydro-2, 2-dimethyl-7-hydroxybenzofuran (7-OH) with MIC in an enclosed batch reactor. Methylene chloride is used as a coolant to control the reaction rate. After completion of the batch reaction, vapors including unreacted MIC are purged

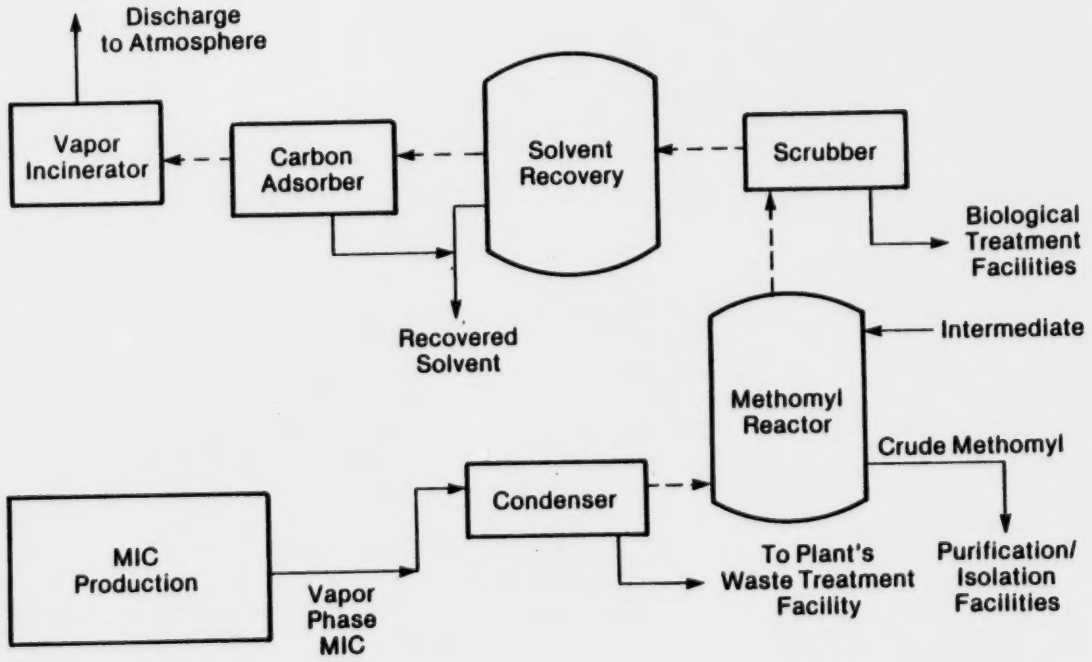

Figure 3-5. Methomyl (LANNATE®) production at DuPont's Laborte, Texas Facility.

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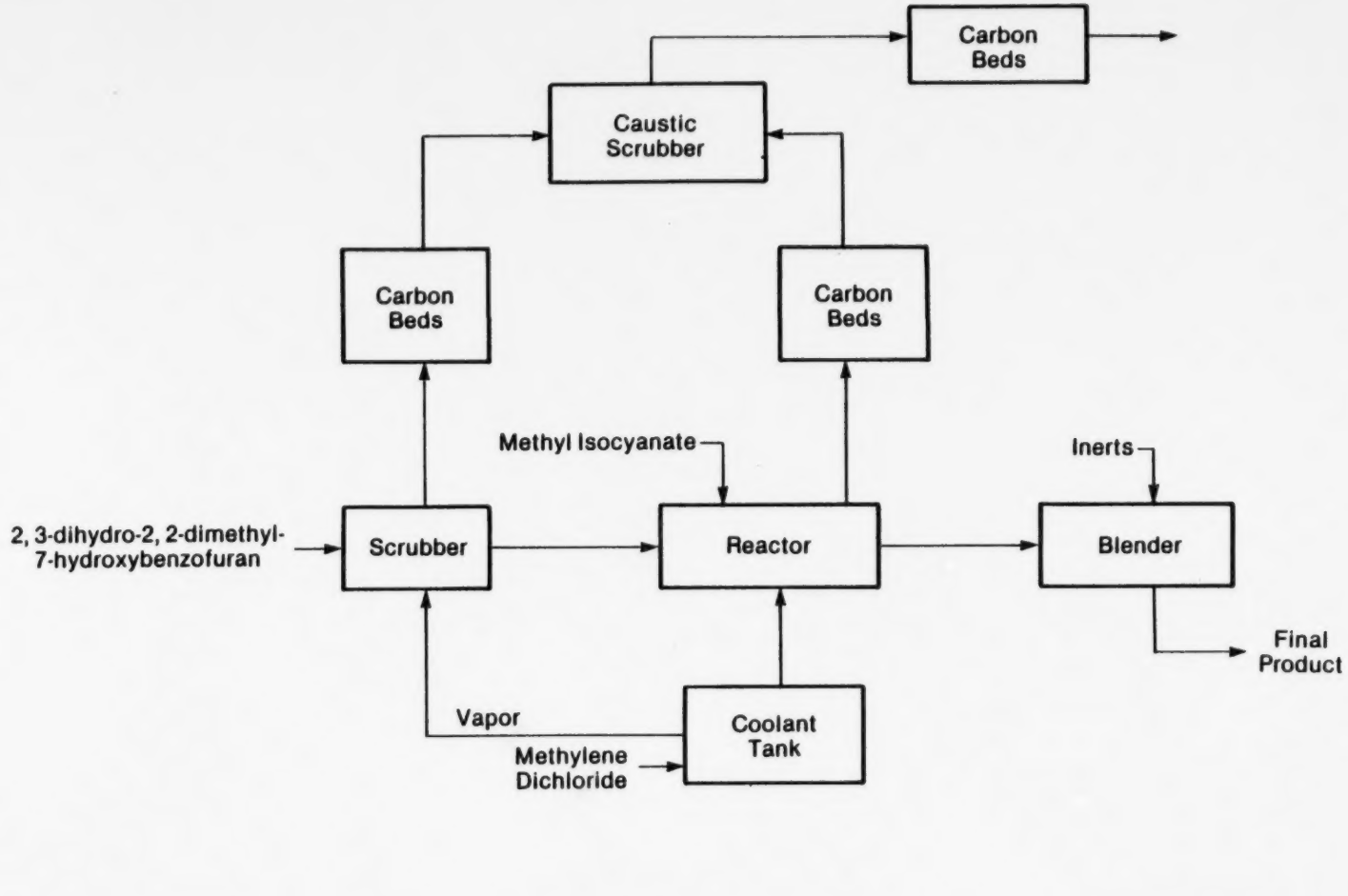

Figure 3-6. Carbofuran (FURADAN®) production at FMC's Institute, West Virginia Facility.

from the reactor by a combination of vacuum and purging operations with nitrogen. Most of the MIC and methylene chloride vapors are condensed and recovered in the coolant tank. MIC vapors which are not condensed in the condenser are vented to the 7-OH scrubber where they react to form carbofuran. The recovered MIC and methylene chloride are recycled to the reactor. Process gases from the 7-OH scrubber are vented to a carbon adsorber followed by a caustic scrubber. Pressure relief devices from the reactor are vented to a carbon adsorber and caustic scrubber as well. According to FMC, the scrubber has an efficiency of 99.9 percent.

SECTION 4
PROCESS HAZARDS

4.1 HISTORICAL PERSPECTIVE

This section provides a brief description of major hazards associated with the manufacture and use of MIC. Preventive measures associated with these hazards are discussed in Section 5.

There are two basic causes of releases of MIC: 1) uncontrolled chemical reactions; and 2) spills and/or leaks that may occur during normal operations, such as routine maintenance and cleaning of equipment.

4.1.1 Uncontrolled Chemical Reactions

Uncontrolled chemical reactions involving MIC are extremely dangerous. An uncontrolled chemical reaction involving MIC could cause a release creating an immediate and catastrophic hazard that may affect the general public along with plant personnel. There is no evidence that an accidental release of MIC resulting from an uncontrolled reaction has ever occurred in a United States facility. However, the release of 10,000 gallons of MIC in Bhopal, India in December 1984 shows that there is a potential for releases from MIC facilities. That release resulted from an uncontrolled reaction in a storage vessel.

4.1.2 Spills and/or Leaks

The MIC released as a result of spills and/or leaks is not expected to be as great as that resulting from a runaway reaction. However, there is probably a larger potential for spills and/or leaks that may occur during normal operations, such as routine maintenance and cleaning of equipment. A total of 67 such releases of MIC were reported to have occurred at three

facilities which consume or produce MIC (2,15,21). Some of these releases occurred at MIC-user facilities that are no longer in operation. The majority of MIC releases were the result of equipment failures. There were also several reported incidents where releases of MIC resulted from residual MIC in lines opened for repair. The quantity of MIC released ranged from less than 1 ounce to slightly greater than 10 pounds (a little more than one gallon).

No fatalities or injuries have been attributed to a release of MIC in the United States. One incident did occur involving a release of MIC that sent eleven people to the hospital. The release on November 15, 1984 at FMC in Middleport, New York was due to a pump failure and resulted in the evacuation of nearby areas including a school. Nine children and two adults were treated for eye irritation at a local hospital.

4.2 POTENTIAL CAUSES OF RELEASES

Failures leading to accidental MIC releases, due to both uncontrolled reactions, spills and/or leaks, may be broadly classified as due to process, equipment or operational causes. This classification is for convenience only. Causes discussed below are intended to be illustrative, not exhaustive. A more detailed discussion of possible causes of accidental releases of toxic chemicals in general, which also applies to MIC is presented in the Control Technology volume of the prevention reference manual series of which this manual is a part.

4.2.1 Process Causes

Process causes are related to the fundamentals of process chemistry, control, and general operation. Possible process causes of an MIC release include:

- Contamination of MIC due to rust from nitrogen supply line resulting in a runaway reaction;

- Contamination of MIC due to backflow of caustic solution from scrubber resulting in a runaway reaction;
- Contamination of MIC due to brine which may be used as a cooling fluid resulting in a runaway reaction;
- Insufficient monitoring equipment (e.g., temperature, pressure) for detecting process upsets or failure of instruments;
- Improper design of control devices (e.g., scrubber, flare) to neutralize MIC emissions due to process upsets or failure of control systems; and
- Insufficient cooling capacity to control MIC storage temperature or failure of cooling system.

4.2.2 Equipment Causes

Equipment causes of accidental releases resulting from hardware failure. Some possible causes include:

- Improper material of construction such as iron, aluminum, ordinary carbon steel or copper which act as a catalyst causing a highly exothermic reaction;
- Improper material of construction (e.g., synthetic products) which dissolve in MIC;
- Power failure with no alternative power source resulting in a failure of the MIC cooling system;
- Failure of equipment (e.g., pumps, pressure relief valves) with no back-up system;
- Excessive mechanical stress due to improper fabrication, construction, or installation;
- Failure of vessels at normal operating conditions due to weakening of equipment from excessive mechanical stress, external loadings, or corrosion; and
- Mechanical fatigue and shock in any equipment. Mechanical fatigue could results from age, vibration, or stress cycling caused by pressure cycling, for example. Shock could occur from collisions with moving equipment such as cranes or other equipment in process or storage areas.

4.2.3 Operational Causes

Operation causes of accidental releases are a result of incorrect operating and maintenance procedures or human errors (i.e., not following correct procedure). These cases include:

- Overfilling of storage vessels;
- Neglecting to purge process lines with nitrogen before making repairs;
- Inadequate maintenance in general, but especially on pressure relief systems and other preventive and protective systems:
- Lack of inspection and non-destructive testing of vessels and piping to detect corrosion weakening;

- Incomplete knowledge of the chemical properties, reactivity, and chemical process, involving MIC; and

- Incomplete disaster plan.

SECTION 5
RELEASE PREVENTION AND CONTROL

The previous section identified the causes of accidental releases of MIC. Uncontrolled reactions represent the greatest potential for large releases of MIC. Spills and/or leaks have a higher potential of occurrence, but represent a much smaller quantity of released material. The hazards of any release of MIC are similar. This section addresses the control of releases and the prevention of the causes.

5.1 BACKGROUND

Prevention of accidental releases relies on a combination of technological, administrative, and operational practices. These practices apply to the design, construction, and operation of facilities where MIC is produced, stored and used. Considerations in these areas can be grouped as follows:

- Process design and operational considerations;
- Physical plant design considerations;
- Operating and maintenance practices; and
- Protective systems.

In each of these areas, specific factors must be considered that could lead to a process upset or failure which could directly cause a release of MIC to the environment, or result in an equipment failure which could cause the release. At a minimum, equipment and procedures should be examined to ensure that they are in accordance with applicable codes, standards, and regulations.

In addition, stricter equipment and procedural specifications should be in place if extra protection against a release is considered appropriate.

In Section 4, 67 releases of MIC were reported for three facilities that produce or consume MIC. Most of these releases, though small, were the result of equipment failure. Therefore, it is important to consider process design and operation in assessing potential releases. Other releases reported were the result of MIC remaining in equipment and lines opened for repair. These releases are associated with operating and maintenance practices. The fatal release in Bhopal relates to all of these aspects.

The following subsections discuss some specific considerations regarding release prevention as they relate to each of the areas mentioned above. More detailed discussions on each of these areas will be found in a manual on control technologies included in this manual series.

5.2 PROCESS DESIGN AND OPERATION

Process design and operational considerations involve fundamental characteristics of the processes which produce or use MIC. Each unit operation must be evaluated to consider if deviations from design might initiate a series of events that could result in an accidental release. Process control must be considered in terms of the basic process chemistry involved, and the following control parameters: flow, pressure, temperature, composition, and level. Additional considerations may include process control instrumentation, metering systems, mixing systems, and fire protection. Modifications to enhance process integrity may result from review of these factors and would involve changes in quantities of materials used, process pressure and temperature, the unit operations used, sequence of operations, the process control strategies, and instrumentation used.

Union Carbide made a thorough investigation into the Bhopal release, considering what had caused the large accidental release. The Occupational

Safety and Health Administration (OSHA) inspected all MIC producing and using plants to assess the potential for releases. A joint Federal-State Task Force investigated the potential for release at the Institute, West Virginia MIC unit. The Task Force considered a variety of aspects of process, chemistry, process control, and environmental controls. Table 5-1 presents the summary of the Task Force evaluation of equipment (10).

The investigatory work noted above pointed to the major areas of concentration for this study:

- Design measured to prevent the likelihood of MIC contamination;
- Sufficient cooling of MIC in process vessels:
- Minimization of MIC inventory; and
- Sufficient instrumentation and monitoring to provide early detection of possible process upsets.

The most important design considerations are aimed at preventing the likelihood of an uncontrolled reaction involving MIC. Such a reaction could be initiated by contamination from water, strong bases, and certain metal chlorides. Additional information on potentially undesirable reactions involving MIC are presented in literature (4).

Due to the extreme reactivity of MIC, it should always be handled and stored in a protective environment. Many metals such as carbon steel, iron, and aluminum commonly used by the chemical industry could act to catalyze a rapid trimerization that could create a dangerous situation with the heat release. According to literature, UCAPCO recommends that MIC be stored and handled in stainless steel, types 304 and 316; nickel; and glass-lined equipment (4). Glass-lined steel should be carefully evaluated to insure that it is free of pinholes.

TABLE 5-1. ENGINEERING/INSTRUMENTS ASSOCIATED WITH SAFETY SYSTEMS

Equipment	Purpose of Equipment	Redundancy	Warning System
1. Temperature sensors for MIC storage tank.	One of the first indicators of a reaction which could become a runaway reaction is a temperature rise in the storage tanks since water contamination initiates an exothermic reaction.	Yes	Each thermocouple sets of an alarm if the temperature reaches 2°C. If the temperature continues to rise, another alarm is set off at 5°C. The alarms are in the control room.
2. Computer software to monitor rate of temperature rise in storage tanks.	Some temperature fluctuation is normal, however, water contamination would cause a a greater rate of change than	Yes	Each thermocouple sets off an alarm if the rate of temperature change is greater than 0.5°/hour. The alarm is in the control room.
3. Pressure monitors in storage tanks.	If a reaction which could become a runaway reaction were to begin, another indicator would be a rise in tank pressure due to increased temperature and reaction by-products.	Yes	Both pressure sensors are set to start alarms if the tank pressure reaches 2 psi and 10 psi. The alarm is in the control room.
4. Liquid level monitors for storage tanks	The liquid level monitors prevent overfilling the storage tanks.	Yes	The liquid level indicators are connected to alarms and also have an automatic shut-down for the feed and recirculation lines with each tank. The alarm is in control room.

TABLE 5-1. ENGINEERING/INSTRUMENTS ASSOCIATED WITH SAFETY SYSTEMS (continued)

Equipment	Purpose of Equipment	Redundancy	Warning System
5. Refrigeration system for storage tanks.	It is important to try to keep stored MIC at low temperatures since the reaction rate of MIC is dependent on temperature. Increased refrigeration is one of the first corrective actions taken if contamination is suspected.	Yes	Not applicable.
6. Devices to assure that flare is always operating: - dual pilot lights - dual thermocouple flame detectors - automatic pilot relight - manual pilot system - temperature interlock with scrubber which automatically actuates emergency gas	The flare is one of the critical control devices to minimize MIC losses to the atmosphere if an uncontrolled reaction were to generate large amounts of MIC vapors and gases from the storage tanks. Therefore it is important that the flare always be in operation and these devices are designed for that purpose.	Yes (for ignition systems and back-up gas supplies)	Alarm systems in control room.

TABLE 5-1. ENGINEERING/INSTRUMENTS ASSOCIATED WITH SAFETY SYSTEMS (continued)

Equipment	Purpose of Equipment	Redundancy	Warning System
7. Safety valves for storage tanks	The safety valves on the storage tank relieve the build-up of pressure by venting the gas to the scrubber and flare that results from an uncontrolled reaction. The safety valves have been redesigned and replaced so that the release of MIC gases would be better controlled by the scrubber and flare. In addition, the flares can be manually operated with an air operated remote control system which can over-ride normal operating conditions in case it is needed. This operation would be performed from the control room. The valves are also equipped with rupture disks to prevent back-flow of caustic to the valves and tanks.	There is only safety valve per tank. However, manual operation, capability of liquid disposal to scrubber, and frequent inspections add to the reliability of the safety.	Pressure transducer between safety valve and rupture disk would show increased pressure.
8. Emergency vent gas	This equipment is designed to neutralize MIC vapors or liquid if they were to be released or pumped from the storage tanks. Certain design changes to increase the capacity for neutralization of MIC have been made. The scrubber is continuously running.	(1) Duplicate circulation pumps for scrubber (2) Additional caustic storage capacity (3) Access to reserve caustic	(1) High caustic temperature activates an alarm in the control room and converts the caustic circulating system to a one-pass mode. Additional caustic is added. (2) Pump motor alarm would indicate malfunction of scrubber caustic circulation system.

TABLE 5-1. ENGINEERING/INSTRUMENTS ASSOCIATED WITH SAFETY SYSTEMS (continued)

Equipment	Purpose of Equipment	Redundancy	Warning System
9. Utilities: - electric - instrument air - cooling water	To provide power to run the equipment and critical instruments.	All utilities have back-ups. Back-ups include: - steam driven - alternative fuel sources - nitrogen for instrument air - separate electrical substations - stand-by generators	Not applicable
10. MIC transfers lines: - pumps - check valves - low flows shut offs - nitrogen purging for clearing and and drying lines	The MIC transfer lines are designed with certain safety features to prevent pump overloads, back-flows, low-flows. The transfer lines have automatic shut-off valves to prevent backflows to the tanks and to stop continued flow in case of transfer line rupture.	Not applicable	Pumps have amp meters and alarms for overload or failure.
11. Control valve fail-safe remain	All control valves would remain in the most conservative position regarding safety in case of electrical failure.	Not applicable	Valve positions indicated in control room.

Additional precautions include preventing MIC contact with air. This is due to the highly exothermic reaction of MIC with water vapor and the possibility of combustion in the presence of oxygen. The danger can be reduced by the use of a nitrogen blanket during storage, transfer operation, or whenever there is a possibility of exposure to air. Cooling of MIC storage and process tanks is recommended to limit the reactivity and volatility at higher temperatures. MIC should be stored below 59°F, preferably as low as 32°F. Cooling can be performed by coils on the outside walls of the storage tanks or by circulating MIC through a heat exchanger. In the past, coolants such as brine, chloroform and methylene chloride have been used as cooling fluids. Because there is a risk of contamination with subsequent trimerization and heat release, brine is no longer used a cooling fluid.

At UCAPCO's Institute plant, chloroform has replaced brine at the cooling fluid. Chloroform is unreactive with MIC and, in fact, is even used as a solvent in the process. Use of chloroform as the heat transfer fluid eliminates one potential for runaway reaction due to contamination. Coolant system failure also creates a potential for temperature increase and subsequent runaway reaction. UCAPCO has done several things to reduce this potential. The circulation pumps are spared, one operating on electricity, the other driven by steam. Local authorities are now notified if cooling capacity is reduced or lost when MIC is in storage.

Since potential risk from MIC increases with the amount of MIC in storage, inventories should be kept to a minimum. While a high inventory of MIC could be advantageous from a marketing perspective, the potential hazards should be carefully evaluated in determining the amount of MIC to be stored at a facility. UCAPCO maintains several MIC storage stanks: 3 make tanks of 14,000 gallons each, 3 underground tanks of 30,000 gallons each, 1 relief tank of 30,000 gallon capacity, one 7,000-gallon process tank for Larvin production, and one 8,500-gallon relief tank in the same unit. One make tank and one underground tank are maintained empty, ready for use for excess or off-specification materials. Four other tanks have been removed from service.

Another option to reducing inventories of MIC is a change in production route. The two other plants producing MIC in the U.S. use processes that consume the MIC as quickly as it is produced. This route allows the elimination of MIC storage to feed the pesticide process. In addition, by using the MIC as quickly as it is produced, there is no intermediate storage of MIC required.

An additional area of process design is instrumentation and monitoring to provide early detection of possible process upsets. All process vessels should be equipped with pressure, temperature, and liquid level indicators. A sudden change in any of these parameters indicates a potential process upset or an undesirable reaction. Monitors of control equipment should be centrally located. Monitoring equipment should also be equipped with alarms to indicate a sudden change or abnormal reading of pressure or temperature.

An example of instrumentation requirements is illustrated in Figure 5-1. This figure shows a double-wall underground storage tank for MIC, cooled using a recirculation loop. The recirculation pump is monitored by an ammeter. If the motor trips or begins to labor, an alarm notifies the operator of potential dangers. Tank pressure and liner pressure are both monitored. In the event of rapid vaporization and pressure increase, an alarm signals an eminent pressure relief valve discharge. Storage tanks are also monitored for temperature and inventory (level). Pressure and inventory monitors are both redundant. The Task Force found the Institute plant to be adequately instrumented to give proper notification of potential releases. Vents from storage and process vessels, if a release does occur, are routed to a well-designed control system.

5.3 PHYSICAL PLANT DESIGN

Physical plant design considerations include equipment, siting and layout, and transfer/transport facilities. Vessels, piping and valves, process machinery, instrumentation, and factors such as locations of systems

and equipment must all be considered. The following subsections cover various aspects of physical plant design.

5.3.1 Equipment

Materials of Construction--

Due to the extreme reactivity of MIC, it should always be handled and stored in a protective environment. Many metals, such as carbon steel, iron, tin and aluminum are commonly used by the chemical industry but could act to catalyze a dangerously rapid trimerization of MIC. The induction period for materials catalyzing MIC reactions ranges from several minutes for sodium methoxide to several weeks for 4-dimethylaminopyridine. UCAPCO recommends that MIC be stored and handled only in stainless steel, types 304 and 316; nickel; and glass-lined equipment. Glass-lined steel should be free of pinholes. The Institute plant uses stainless steel vessels and piping.

Vessels--

Vessels in MIC service in the United States include storage tanks, reaction vessels, and distillation columns. For safety reasons, storage vessels are typically designed for twice the volume required. The extra volume allows space for adding an inert diluent such as chloroform to act as a heat sink. This would not stop a runaway reaction but it would slow down such a reaction to allow alternative action measures to be taken. UCAPCO recommends a maximum filling capacity of 80 percent (12). As an alternative, an empty storage tank, free of air and moisture, could be maintained at all times. Should an in-use storage tank become contaminated with water or a salt or other compound, part or all of the contents could be transferred to the empty standby storage tank. An additional safety measure taken by UCAPCO is the use of double wall construction of their underground storage tanks. This allows for environmental protection and the ability to monitor for leaks, as shown in Figure 5-1.

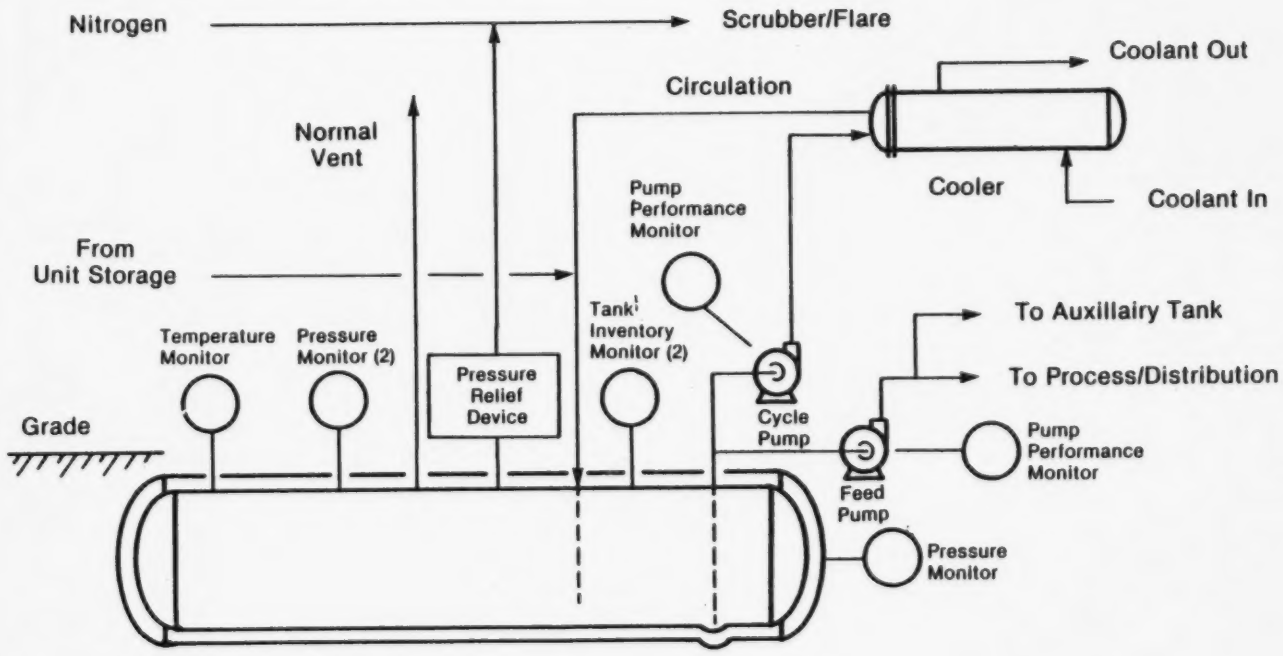

Figure 5-1. Typical underground storage installation.

Piping--

As with MIC vessels, MIC piping design must reflect the pressure, temperature, and corrosion concerns associated with MIC. Piping should be simple in design; the number of joints and connections should be minimized. Consistent with good plant design, piping should be constructed to allow for thermal expansion of the pipe and should be placed from exposure to fire and high temperatures. Valves should be placed so that leaking pipes and equipment may be isolated from service for repair. No section of piping should be totally isolated from some form of overpressure relief or expansion chamber, so that any releases can be treated in the caustic scrubber/flare system.

Another consideration must be made with respect to piping systems. With any piping arrangements, the potential for hydrostatic pressure releases exists if the piping is blocked in, liquid full. This situation is especially true of pipelines, such as those from storage vessels to process units using the material. Relief to treatment/control systems should be installed on such pipelines.

Pumps--

Many of the concerns and considerations for MIC piping also apply to pumps. For example, positive displacement pumps should not be deadheaded to avoid releases. To assure that a given pump is suitable for MIC service, the system designer should obtain information from the pump manufacturer certifying that the pump will perform properly in this application.

Pumps should be constructed with materials which are resistant to MIC at operating temperatures and pressures. Net positive suction head (NPSH) considerations are especially important for MIC since pumping the liquid near its boiling point may be common. The pump supply tank should have high and low level alarms; the pump should be interlocked to shut off at a low supply level or low discharge pressure.

In many cases, the potential for seal leakage rules out the use of rotating shaft seals. One solution is to use pump types which limit the potential seal leakage from the process stream. The more popular solution is to use pump types which eliminate shaft seals altogether such as canned-motor, vertical extended-spindle submersible, magnetically-coupled, and diaphragm. Canned pumps are in use in MIC production.

Canned motor pumps are centrifugal units in which the motor housing is interconnected with the pump casing. The process liquid actually serves as the bearing lubricant. An alternate concept is the vertical pump often used on storage tanks. Vertical pumps consist of a submerged impeller housing connected by an extended drive shaft to the motor. The advantages of this arrangement are that the shaft seal is above the maximum liquid level (and is therefore not wetted by the pumped liquid) and the pump is self priming because the liquid level is above the impeller.

Magnetically-coupled pumps replace the drive shaft with a rotating magnetic field as the pump-motor coupling device. Diaphragm pumps are positive displacement units in which a reciprocating flexible diaphragm drives the fluid. This arrangement eliminates exposure of packing and seals to the pumped liquid.

5.3.2 Plant Siting and Layout

Currently, there are four companies processing MIC in the United States. DuPont and Sandoz in Texas consume MIC as quickly as it is produced, therefore layout of the site is less critical than for units storing the material. UCAPCO produces much more MIC and stores the material for use at FMC and other UCAPCO units at the Institute manufacturing site. The use of underground storage tanks was considered in the Task Force study and was found to be adequate with existing controls. The remainder of this subsection is cogent to the Institute facility and to new installations.

The siting and layout of a particular MIC facility is a complex issue which requires careful consideration of numerous factors. These include: other processes in the vicinity, the proximity of population centers, prevailing winds, local terrain, and potential natural external effects such as flooding. The rest of this subsection describes general considerations which might apply to siting and layout of MIC facilities.

Siting of facilities or individual equipment items should be done in a manner that minimizes personnel exposure, both plant and public, in the event of a release. Since there are also other siting considerations, there may be trade-offs between this requirements and others. The site should provide ready ingress or egress in the event of an emergency and yet take advantage of barriers, either man-made or natural, which could reduce the hazards of releases. Large distances between large inventories and sensitive receptors is desirable.

Layout refers to the placement and arrangement of equipment in the process facility. Some general layout considerations include the following:

- Large inventories of MIC should be kept away from sources of fire or explosion hazard;

- Vehicular traffic should not go too near MIC process or storage areas if this can be avoided;

- Where such traffic is necessary, precautions should be taken to reduce the chances for vehicular collisions with equipment, especially pipe racks carrying MIC across or next to roadways;

- MIC piping preferably should not be located adjacent to other piping which is under high pressure or temperature, or which carries flammable materials; and

- Storage facilities should be segregated from the main process unless the hazards of pipe transport are felt to outweigh the hazards of the storage tank for site-specific cases.

Because heat increases MIC reactivity, measures should be taken to situate piping, storage vessels, and other MIC equipment to minimize heat exposure. Hot process piping, equipment, steam lines, and other sources of direct or radiant heat should be avoided. Storage should also be situated away from control rooms, offices, utilities, storage and laboratory areas. Special precautions should be taken to keep MIC storage vessels away from potential fire or explosion sources. The above-ground storage tanks at UCAPCO are protected from external forces, such as an explosion at a neighboring process, by a blast net and a water deluge system.

In the event of an emergency, there should be multiple means of access to the facility for emergency vehicles and crews. Storage vessel shut-off valves should be readily accessible. Containment for liquid storage tanks can be provided by diking. Dikes reduce evaporation while containing the liquid. It is also possible to equip a diked area to allow drainage to an underground containment sump. This sump would be vented to a control system for safe disposal. Such a system at UCAPCO is equipped to handle an MIC spill of up to 42,000 gallons. A full containment system using a specially constructed building vented to a control system is another possible option. For any new installations, this type of secondary containment should be considered for large volume, liquid MIC storage tanks. However, there are secondary hazards with such a system, and extreme care in layout and design are required to protect the operators.

5.3.3 Loading and Unloading Facilities

In the past, loading and unloading facilities were likely accident areas because of vehicle movement, operator practices, and the intermittent nature of the operation. However, this has changed significantly in the past five

years. All bulk shipments of MIC have been eliminated. Only small samples used for research purposes are shipped. These samples total approximately 50 to 100 gallons per year with no more than 1 gallon per shipment (22).

5.4 PROTECTION TECHNOLOGIES

This subsection describes the types of protection technologies in effective use for containment and neutralization at MIC facilities. These technologies were presented in Section 3:

- Enclosures;
- Scrubbers;
- Flares; and
- Other secondary control systems.

A presentation of more detailed information on these systems is planned in other portions of the prevention reference manual series.

5.4.1 Enclosure

Enclosures refer to containment structures which capture any MIC spilled or vented from storage or process equipment, thereby preventing immediate discharge of the chemical to the environment. The enclosures contain the spilled liquid or gas until it can be transferred to other containment, discharged at a controlled rate which would not be injurious to people or the environment, or transferred at a controlled rate to scrubbers for neutralization. UCAPCO has an underground enclosure capable of collecting 42,000 gallons.

The desirability of enclosure depends partly on the frequency with which personnel must be involved with the equipment. A common design rationale for not having an enclosure where toxic materials are used is to prevent the accumulation of toxic concentrations of a chemical within a work area. However, if the issue is protecting the community from accidental release, then total enclosure may be appropriate. Enclosures should be equipped with continuous monitoring equipment and alarms. Alarms should sound whenever lethal or flammable concentrations are detected.

The containment structures that appear to be suitable for MIC are preferably gas tight and have a ventilation system designed to draw in air when the building is vented to a scrubber. The bottom section of a building used for stationary storage containers should be liquid tight to retain any liquid MIC that might be spilled.

5.4.2 Scrubbers

Scrubbers are a traditional method for removing toxic gases from process streams. These devices can be used to control MIC released from process vents and pressure relief discharges from storage and process equipment.

Due to extreme reactivity with caustic, MIC is destroyed rather than absorbed by a scrubber. MIC reacts with a caustic solution to produce urea compounds. Scrubbers used for the purpose of controlling MIC emissions are designed using two principles. First, the scrubber is designed to convert any emissions that may be associated with the processing of MIC. Secondly, the scrubber is designed to neutralize MIC emissions should a catastrophic or worst-case event occur. The worst-case scenario adopted by UCAPCO in their scrubber design is based on a runaway reaction in their largest storage tank. This scenario assumes the following series of events: 1) the MIC in one of the 30,000-gallon storage tanks is contaminated with water at the limit of solubility at ambient conditions, 2) the refrigeration and back-up refrigeration systems of the tank have failed, and 3) it is not possible for some mechanical

reason to transfer the MIC for destruction. Although highly improbable, an even worse case scenario might be possible, if more than one tank could be contaminated at the same time, or that a tank could be contaminated by caustic or other material, which would react faster than water.

Water and caustic contamination of MIC storage tanks is possible. It is one of the suspected causes of the large MIC release at Bhopal. Check valves are used extensively to avoid back flow from the scrubber to the storage tanks. In addition, the feed nozzle configuration in the scrubber has been modified to prevent backflow of caustic solution into the storage tank.

Scrubber designs at both DuPont in LaPorte, Texas and Sandoz, in Beaumont, Texas are also based on the worst-case event. Both these facilities manufacture MIC as a captive intermediate with no storage; MIC is consumed as it is produced. The worst-case scenario for these two facilities assume that all MIC is sent directly to the scrubber as it is produced. This event would occur if the reaction to product was entirely stopped.

In the design of the UCAPCO scrubber (packed column), several key issues were considered to insure its effectiveness during an extreme-case event.

These issues include:

- Flooding occurs when the gas flow rate to the scrubber becomes too high, preventing the caustic from flowing through the packing and reacting with the MIC.

- Sufficient caustic solution and circulation should be available to control both peak emission rates and total MIC emissions during an extreme event. To help mitigate these situations, the caustic storage capacity has been increased by 70,000 gallons, increased liquid residence time at the base of the scrubber, and added control to maintain caustic at 10 percent during emergency operations.

- The increase in scrubber temperature due to the exothermic caustic-MIC reaction could decrease scrubber efficiency.

- Sufficient amount of contact between MIC vapor and caustic solution should be available to insure neutralization.

The Task Force examined all of these factors and determined that the scrubber at UCAPCO's Institute plant is sufficiently large to control the worst-case emissions from a storage tank. Their analysis estimated the scrubber control efficiency at over 99.9 percent.

5.4.3 Flares

Flares are routinely used in the chemical process industries to dispose of intermittent or emergency emissions of flammable waste gases. Flares, used in the control of MIC emissions, serve as a secondary or back-up control device. As in the design of scrubbers, flares should also be designed to operate effectively during the course of a worst-case event such as the failure of the primary control device (scrubber). Union Carbide has taken several measures to insure proper operation of the flare for controlling MIC emissions. The measures include:

- Dual pilot lights;

- Dual thermocouple flame detectors;

- Automatic pilot relight system; and

- Temperature interlock with scrubber which automatically activates emergency gas.

5.4.4 Other Secondary Control Systems

Aside from caustic scrubbers and flares, additional control techniques are currently in service for the reduction of possible releases of MIC. These control techniques include carbon adsorption used by DuPont and FMC, and vapor incineration used by DuPont. In all cases, these control techniques are used as a secondary control device, with a caustic scrubber being used as the primary control device.

5.5 MITIGATION AFTER RELEASE

Once MIC has been released to the atmosphere, the primary concern becomes reducing the consequences to the plant and the surrounding community. Mitigation technologies include such measures as physical barriers, water sprays, activated carbon for liquid spills, evacuation procedures, and community preparedness. Mitigation technologies for MIC releases discussed in this section disperse, limit, and/or destroy the toxic chemical that has been released to the atmosphere.

Physical barriers may be specially constructed for another purpose but function as barriers, or they may be natural terrain features. An example of a specially constructed structure is a diversion wall. A functional barrier could be a building. A natural terrain feature that might be a barrier is a hill or a line of trees. The primary function of a physical barrier is to protect especially sensitive receptors and provide additional time in which to respond to the accidental release emergency. A physical barrier strategically located can also contribute to enhancing the dispersion of the released chemical. Physical barriers do not, however, directly capture or neutralize the chemical. They might improve the performance of other mitigation measures such as water sprays, however. Applicability and overall performance depend on the nature of a specific release and on the meteorological conditions at the time of the release.

Water sprays, steam curtains and additional methods increase the dispersion rate of the released MIC, direct its direction, serve as a barrier between the toxic, cloud or plume and potential receptors, and, most of all, neutralize the released MIC. As employed by UCAPCO, the water can be applied to the vapor cloud by means of hand-held hoses and or stationary water-spray barriers. To be effective, it is important to direct steam or water spray barriers from a downwind direction to avoid driving the vapors downwind more quickly. Other important factors relating to the effectiveness of water sprays are the distance of the nozzles from the point of release, the fog pattern, nozzle gallonage, pressure, and nozzle rotation. If the right strategy is followed, a "capture zone" can be created downwind of the release into which the MIC vapor will drift and be neutralized.

The severity of a liquid release of MIC can be reduced by the use of activated carbon. This technique is primarily for small spills of up to about five gallons. A sufficient supply of activated carbon should be kept on hand. The depth of carbon should be six inches for each one-inch depth of released liquid.

An alternate measure is to flush the spill with copious amounts of water. This will allow the MIC to react to form harmless ureas. Water can also act, however, to increase the vaporization rate of a spill and spread the MIC over larger areas. For small leaks of MIC, carbon as described above may be a better mitigation method.

Particular attention should be paid to protective clothing should an operator be required to come in contact with MIC vapors and liquids. Several studies have been made to determine the most appropriate form of breathing apparatus and clothing that would be best suited for such exposures (23, 24). Because of MIC's high toxicity and lack of warning properties and because no effective end of service life indicator is currently available, the use of air purifying respirators is not recommended. The best form of protection if

forced to work amidst MIC vapor or liquid spills is a totally encapsulating suit with a self-contained breathing apparatus inside the suit.

Additional mitigation measures involve evacuation procedures. This includes the ability to track a cloud of MIC based on meteorological data and air sampling data and the identification of critical impact areas such as schools, hospitals, and residential areas. An excellent example of these mitigation measures is illustrated by UCAPCO's Institute, West Virginia facility. UCAPCO recently installed a site-specific air plume dispersing modeling system known as SAFER. The system is a minicomputer-based mathematical model with real time data input of wind direction, wind speed, and other weather data from the plant meteorological tower. These data are used by the computer to predict concentration and location of receptors after a release. The computer also calculates the direction of the plume, rate of travel and displays the plume location on a map of the area around the site. Critically impacted areas in the community are highlighted, thus, allowing for notification and evacuation in advance of the plume impact with the community.

In addition to UCAPCO's dispersion modeling system, UCAPCO has installed several detectors for low levels of MIC. The detectors are intended to serve as a back-up should a leak go unnoticed by plant personnel (i.e., irritation of operators' eyes and olfactory system). These detectors are designed to sense MIC at concentrations as low as 0.1 ppm.

Perhaps the most important mitigation technology is the development of specific plans in coordination with local, State, and Federal agencies. Such plans would include specific circumstances which would be considered an emergency, and identification of actions to be taken, including outside agencies to contact in the event of an emergency. UCAPCO's plans call for routine interactions with local authorities to review energency procedures. In addition, the plans at UCAPCO call for notifying local officials if certain conditions persist in the process operation that might lead to an emergency.

5.6 OPERATION AND MAINTENANCE PRACTICES

Accidental releases of toxic materials result not only from inadequate process design or equipment failure but also from operation deficiencies. Thus, safe operation of plants processing MIC requires competent and experienced managers and staff in addition to a well considered and fully understood system of work.

Employees should be thoroughly educated about the important aspects of handling MIC including: proper handling and storing procedures, hazards resulting from improper use and handling, prevention of spills, cleanup procedures, maintenance procedures and emergency procedures. Well defined and planned practices and procedures can minimize the possibility of an accidental release or its magnitude, if one occurs.

Proper preventive maintenance and modification program should be a normal part of plant operation and design procedures to reduce the chances for an accidental release. Maintenance should be based on a priority system to ensure that the most critical equipment is taken care of first. Strict procedures should apply to process modifications to ensure that modifications do not create an unintended hazard. This would include a hazard analysis and safety audit as part of the design. Inspections and non-destructive testing of vessels, piping, and machinery should be conducted periodically to detect small flaws that could eventually lead to a major release.

5.7 FEASIBILITY OF ADDITIONAL CONTROL

Since the Bhopal incident, numerous changes have taken place to reduce the likelihood of an accidental release of MIC. These changes have been prompted by the concerns from producers and users of MIC, along with various regulatory agencies. All four facilities that produce and/or use MIC have made significant process modifications. These process changes are discussed

in detail in Section 3. A summary of recent modifications are presented below:

- UCAPCO (formerly Union Carbide) - Invested about $5 million on design and safety changes. These include increasing the capacity of control equipment, leak detection system, and computerized system to predict the path concentration of a release of MIC gas.

- DuPont - Replaced their process to eliminate shipping and storage of MIC. This process is estimated at $10-12 million and produces MIC as a captive intermediate.

- FMC - Relocated their MIC facility in Institute, West Virginia, eliminating shipping and storage. MIC is now piped directly from UCAPCO's storage facilities to FMC as it is consumed.

- Sandoz - Replaced their process to eliminate shipping and storage of MIC. This process produces MIC as a captive intermediate.

In all cases, facilities were found to have one to three levels of redundancy in control equipment. In many cases, process design and equipment are considered to be state-of-the-art. Due to the high level of control already in place at facilities handling MIC, no additional controls are recommended in this manual. These facilities have been thoroughly evaluated by the U.S. Environmental Protection Agency, Occupational Safety and Health Administration, and various State and local authorities such as Texas Air Control Board and West Virginia Air Pollution Control Commission.

SECTION 6
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APPENDIX A
GLOSSARY

This glossary defines selected terms used in the text of this manual which might be unfamiliar to some users or which might be used differently by different authors.

Accidental release: The unintential spilling, leaking, pumping, purging, emitting, emptying, discharging, escaping, dumping, or disposing of a toxic material into the environment in a manner that is not compliance with a plant's federal, state, or local environment permits and results in toxic concentrations in the air that are a potential health threat to the surrounding community.

Containment/control: A system to which toxic emissions from safety relief discharges are routed to be controlled. A caustic scrubber and/or flare can be containment/control devices. These systems may serve the dual function of destructing continuous process exhaust gas emissions.

Facility: A location at which a process or set of processes are used to produce, refine or repackage chemicals, or a location where a large enough inventory of chemicals are stored so that a significant accidental release of a toxic chemical is possible.

Hazard: A source of danger. The potential for death, injury or other forms of damage to life and property.

Identification: The recognition of a situation, its causes and consequences relating to a defined potential, e.g. Hazard Identification.

Mitigation: Any measure taken to reduce the severity of the adverse effects associated with the accidental release of a hazardous chemical.

Plant: A location at which a process or set of processes are used to produce, refine, or repackage, chemicals.

Prevention: Design and operating measures applied to a process to ensure that primary containment of toxic chemicals within the equipment intended for normal operating conditions.

Primary Containment: The containment provided by the piping, vessels and machinery used in a facility for handling chemicals under normal operating conditions.

Probability/potential: A measure, either qualitative or quantitative, that an event will occur within some unit of time.

Process: The sequence of physical and chemical operations for the production, refining, repackaging or storage of chemicals.

Protection: Measures taken to capture or destroy a toxic chemical that has breached primary containment, but before an uncontrolled release to the environment has occurred.

Reactivity: The ability of one chemical to undergo a chemical reaction with another chemical. Reactivity of one chemical is always measured in reference to the potential for reaction with itself or have high "reactivity", without reference to another chemical. Usually this means that the chemical has the ability to react with common materials such as water, or common materials of construction such as carbon steel.

Redundancy: For control systems, redundancy is the presence of a second piece of control equipment where only one would be required. The second piece of equipment is installed to act as a backup in the event that the primary piece of equipment fails. Redundant equipment can be installed to backup all or selected portions of a control system.

Risk: The probability that a hazard may be realized at any specified level in a given span of time.

Secondary Containment: Process equipment specifically designed to contain mateirals that has breached primary containment before the material is released to the environment and becomes an accidental release. A vent duct and scrubber that are attached to the outlet of a pressure relief device are examples of secondary containment.

Toxicity: A measure of the adverse health effects of exposure to a chemical.

APPENDIX B

TABLE B-1. METRIC (SI) CONVERSION FACTORS

Quantity	To Convert From	To	Multiply By
Length:	in	cm	2.54
	ft	m	0.3048
Area:	in^2	cm^2	6.4516
	ft^2	m^2	0.0929
Volume:	in^3	cm^3	16.39
	ft^3	m^3	0.0283
	gal	m^3	0.0038
Mass (weight):	lb	kg	0.4536
	short ton (ton)	Mg	0.9072
	short ton (ton)	metric ton (t)	0.9072
Pressure:	atm	kPa	101.3
	mm Hg	kPa	0.133
	psia	kPa	X6.895
	psig	kPa*	(P(psig)+14.696) x(6.895)
Temperature	°F	°C*	(5/9)x(°F-32)
	°C	K*	°C+273.15
Caloric Value; Enthalpy:	Btu/lb	kJ/kg	2.326
	Btu/lbmol	kJ/kgmol	2.326
	kcal/gmol	kJ/kgmol	4.184
Specific-Heat Capacity:	Btu/lb-°F	kJ/kg-°C	4.1868
Density:	lb/ft^3	kg/m^3	16.02
	lb/gal	kg/m^3	119.8
Concentartion:	oz/gal	kg/m^3	
	quarts/gal	cm^3/m^3	25,000
Flowrate:	gal/min	m^3/min	0.0038
	gal/day	m^3/day	0.0038
	ft^3/min	m^3/min	0.0283
Velocity:	ft/min	m/min	0.3048
	ft/sec	m/sec	0.3048
Viscosity:	centipoise (CP)	kg/m-s	0.001

*Calculate as indicated.

Source: Adapted from Reference 22.